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COMPLETE SPECIFICATION

Improvements in Finger Nail Enamel Compositions and production thereof

I, PAUL BAUDECROUX, a Citizen of the French Republic, of 11 bis, Rue de Madrid, Neuilly-sur-Seine, Seine Department, France, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The finger nail enamels known to this time generally consist of a resin-like component (more often than not a cellulose derivative), one or more solvents, and one or more plasticizers. The foregoing composition is little different from the cellulose varnish compositions as widely employed for car bodies, building structures, wood articles, artificial leathers and the like.

One of the common features of known finger nail enamel compositions is their unpleasant smell, injurious to users, particularly manicurists who thus continually work in an incommoding atmosphere. The "varnish" smell is ascribable to volatile solvents and diluents, and also to plasticizers which are components of finger nail enamel compositions, viz. volatile hydrocarbons such as benzene, toluene and xylene, lower alkyl ketones such as acetone and methyl ethyl ketone, dioxane, sulphuric ether, chlorinated hydrocarbons such as carbon tetrachloride, trichlorethylene and the like, methyl alcohol, butyl or amyl acetate, tricresyl phosphate and so on.

Camphor is often present in finger nail enamel compositions, affording a contribution in the unpleasant smell of solvents and diluents in use.

The use of solvents, diluents and plasticizers as above referred to sets a problem of medical order on the commercial scale as also, frequently, on the individual scale. As a matter of fact, solvents, diluents and plasticizers as employed in plastics and varnishes are actual toxic agents capable of causing functional perturbations in so far as a predetermined threshold of concentration in ambient air is reached. They produce an anæsthetic effect, act on lungs and central nervous system, and are capable of attacking cellular colloids. Some

of them are keratolytic or keratoplastic. Those solvents, diluents and plasticizers are unsafe to handle on a commercial scale and even on an individual scale, where persons by reason of their occupations are exposed continually to breathe such poisons. Furthermore in not unfrequent cases of allergy in respect of conventional solvents, diluents and plasticizers for finger nail varnishes, the use of finger nail varnishes may be completely forbidden for fear of severe accidents.

It has already been endeavoured to palliate the inconvenience of bad smell in finger nail enamels, by disguising the odor with that of a perfume, for example by adding minute amounts of bergamot oil. The results were very imperfect, the proper smell of conventional solvents, diluents and plasticizers being much too strong.

It is an object of my invention to provide new finger nail enamel compositions which unlike prior compositions as above referred to, have a pleasant perfume smell.

A further object is to provide finger enamel composition containing odoriferous solvents and plasticizers for fingernail enamel cellulose esters and resins, which have not been incorporated as yet in finger nail enamel compositions as solvents and the like, but are found to be valuable in that respect.

Another object is to provide a finger nail enamel composition which is not liable to blushing even though it may contain water.

Further objects and advantages of my invention will appear as the specification proceeds.

In the succeeding description parts by weight to parts by volume has the same ratio as grams to cubic centimetres.

The present invention comprises a finger nail enamel composition obtained by mixing together components comprising 10—30 parts by weight of a film-forming base which is a cellulose derivative or a mixture of a cellulose derivative and a resin, about 10—30 parts by volume of a mixture of at least two odoriferous substances compounded into a perfume providing a solvent for the film-forming base, the major portion of said mixture consisting of

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substances which have not less than 7 carbon atoms and contain at least one methyl group and are selected from the class of esters, aldehydes, ketones, alcohols and essential oils, and about 40—80 parts by volume of a diluent which is an aliphatic alcohol having from 2 to 4 carbon atoms, or a propionic acid ester.

Any one of the conventional film-forming bases for finger nail enamel compositions may be employed, preference being given to nitrocellulose as the cellulose derivative component of the base. However acetocellulose for example may also be employed. The preferred nitrocellulose is of the soluble pyroxylin type, containing from about 11.2 to about 12.2 per cent nitrogen, particularly the grade having a viscosity designation of 0.5 second. The film-forming base preferably employed further comprises a resin or resins as are usually present in modern finger nail compositions and will be broadly referred to herein as finger nail enamel resins, e.g. natural or modified natural resins (for example rosin, mastic, elemi, ester gum, dammar, sandarac, kauri and the like) and synthetic resins, such as polyvinyl, polystyrene, urea, coumarone and like synthetic resins.

As a solvent for the film-forming base, instead of employing the conventional lower alkyl acetates, singly or in binary mixtures, and/or acetone and the like, I use, according to this invention, a mixture of odoriferous substances compounded into a perfume having a quick rate of evaporation and a pleasant scent, said substances being selected from the class of CH_3 -bearing compounds; a number of at least three components is generally required for obtaining a suitable compound according to a practice similar to the practice of perfume makers, but in the present case, care is to be exercised both to select the components and balance the proportions thereof adequately to have a quick rate of evaporation, unlike the common practice in perfumery where on the contrary fixateurs are desirably added to lower the evaporation rate, and also to produce a pleasant scent.

In addition to the film-forming base, solvent and diluent, a finger nail enamel composition according to this invention may contain one or more plasticizers which are also selected from the class of odoriferous substances.

In so far as lower alkyl acetates are employed as solvent components, they are to be compounded with at least one odoriferous substance having not less than 7 carbon atoms and selected from the class above described to provide a quickly evaporating mixed solvent having a fragrance in which the "varnish" smell of individual lower alkyl acetates cannot be detected.

As already indicated, the major portion of the perfume mixture which provides a solvent of the film forming base consists of substances selected from the class of odoriferous sub-

stances which contain at least 7 carbon atoms, of which at least one is that of a methyl group. I have found that it is desirable for the components to have such a methyl group with a view to providing a mixture which is a solvent for the film-forming base, i.e. both for nitrocellulose or acetocellulose and resins. In so far as odoriferous substances are intended to be employed as plasticizers rather than solvents, it is not necessary for them to have a methyl group in their molecule.

As suitable solvent components and plasticizers, I may mention carboxylic acid esters such as formic, ortho-formic, acetic, propionic, butyric, sebacic, oenanthylic, pelargonic, valerianic, benzoic, salicylic, anthranilic, phenylacetic, cinnamic, hydrocinnamic and like acid esters including ethinyl carboxylic acid esters such as methyl ester of heptin and octin carboxylic acid, aldehydes including lower aliphatic aldehydes such as acetaldehyde and butyraldehyde, and aromatic aldehydes such as benzaldehyde, vanillin and heliotropin, ketones, for example acyclic ketones such as methylheptanone, hydrocyclic ketones such as the numerous ketones found in essential oils, hydroaromatic ketones such as irone, ionones, ketones having a large cycle such as muscone and civettone, arylaliphatic ketones such as acetophenone, benzylidene acetone, β -methyl naphthyl ketone, aromatic ketones such as benzophenone aliphatic alcohols and ethers thereof; particularly valuable solvent components are alcohols of the acyclic and cyclic terpenic series as a class and esters, especially lower aliphatic acid esters thereof, e.g. citronellol, rhodinol, geraniol, nerol, linalol and the like, formic, acetic, butyric and like acid esters thereof, citronellal, rodinal, citral, geranial, neral, hydroxy-citronellal; the essential oils also provide suitable solvent components in addition to plasticizers for the film-forming base. The foregoing compounds include typical examples of substances having a CH_3 -group which are solvents for finger nail enamel film-forming bases. Among the numerous compounds which are useful according to this invention, ethyl ortho-formate is particularly desirable.

In particular, I have found that musks as a class are valuable plasticizers, particularly artificial musks (ketone musk, xylene musk, ambrette musk) which are tertiary butyl nitro xylenes; artificial musks have but a poor solubility in alcohol (about 2%); however if properly compounded with the solvent for the composition, they can be added in amounts far above the limit of solubility in alcohol to give a highly plasticized, highly perfumed film. As a source of plasticizers, I may also employ essential oils having a pleasant smell, which generally are also a source of solvents by reason of their chemical composition, e.g. lavender oil, Neroli oil, Cananga oil, Ylang-ylang oil and the like.

As further plasticizers which I found suit-

able, I may mention coumarin, acetyl isoeugenol, menthol, paracresol benzoate, phenyl benzoate, metacresol, phenylacetate, methyl cinnamate, phenylacetic acid, phenyl ethyl salicylate, ethyl naphthalate, benzyl cinnamate, phenyl-ethyl anthranilate, paracresol, diphenylmethane, phenylethyl cinnamate, dimethyl benzyl carbinol acetate, cinnamyl anthranilate, cinnamyl alcohol and anisic alcohol.

- 10 As diluents, I may employ an aliphatic alcohol containing 2—4 carbon atoms per molecule or a propionic ester. I generally prefer ethyl alcohol which need not be employed as absolute alcohol but, on the contrary, is preferably added as commercial alcohol of a strength of about 90—96% by volume. It is unexpected that compositions in accordance with this invention containing more than 40 per cent, usually 50—60% of commercial alcohol, are capable of yielding films absolutely free from blushing in spite of the considerable proportion of water brought in by commercial alcohol. As a matter of fact, I have found that the strength of alcohol is immaterial in that respect but it will be realized that in commercial practice, it is preferred to employ common commercial strengths rather than dilute solutions. While ethyl alcohol is preferred, other aliphatic alcohols having 2—4 carbon atoms or propionic acid esters may also be employed; as examples of other suitable alcohols, I may also mention butyl and isobutyl alcohols which may partly act as true solvents. A particularly desirable diluent which also plays the part of a solvent and an evaporation quickening agent for other components is isobutyl propionate.

Generally speaking it is preferred according to this invention to constitute the whole dissolving and plasticizing phase for the film-forming base, from components selected from the class of odoriferous substances employed heretofore as components of perfumes. As a matter of fact, bearing in mind the boiling point, vapour pressure, specific gravity and viscosity of the components selected from said class, it is possible to compound the same suitably without it being necessary to add solvents and plasticizers as have exclusively been employed up to this time in manufacturing finger nail enamel composition, i.e. chiefly lower alkyl acetates, lower aliphatic ketones, phthalates and camphor.

It will be understood that compounding is so effected as to provide quick evaporation of the mixed solvent and a pleasant fragrance which is that of a perfume instead of the usual cellulose varnish smell.

In particular, it is possible according to this invention to obtain adhering, glossy, resistant, flexible films, the scent of which may be considerably varied by different compounding of odiferous substances such as synthetic esters, aurantiaceae oils, and particular labiate oils

and the like, which have a high content of esters and terpenes that first evaporate because their boiling point is generally fairly low, and produce, if the mixture of solvents in properly balanced, a pleasant characteristic odour distinct from the odours of the constituent substances.

The pleasant background smell can easily be obtained because it is not required to provide a particularly permeable film-forming base for an easier, quick evaporation of "varnish" smell.

It will be appreciated that finger nail enamel compositions according to this invention are actual perfumes the composition of which can be altered to suit fashion requirements without departing from the essential features of this invention.

It has already been proposed to associate organic acid esters of borneol, iso-borneol or terpineol with esters or ethers of carbohydrates, particularly nitrocellulose, for the production of varnishes, enamels, paints as well as coating compositions, and to dilute the pasty mass obtained from such an association, with ethyl, propyl or butyl-alcohol. According to the prior proposal, it was not contemplated to compound the organic acid esters into a perfume and the example illustrating the proposal shows the use of the organic acid esters by a considerably lower amount than the amount of nitrocellulose.

It has further been proposed to provide salve-like or gelatinous preparations suitable for medical, cosmetic or edible purposes, which comprise an aqueous alcoholic solution of acetyl celluloses mixed with a softening agent or with a solvent having a therapeutically active or a perfumatory, with or without a sweetening or other taste-imparting, character. As perfumes having a solvent power for acetyl cellulose, heliotropine is mentioned.

It has also been proposed to treat cellulose esters, particularly nitrocellulose, in the presence or absence of ethyl alcohol or alcohol substitutes with certain camphor substitutes or solvents, which include (a) etherified derivatives of monophenols, polyphenols and homologues of the same, as well as their nucleus and lateral substitution products, (b) aromatic side chain alcohols and their substitution products and (c) mixtures of the products indicated under (a) and (b) two or more together. It is pointed out that in the manufacture, of celluloid, camphor is usually employed in less amounts than the cellulose ester. However the prior proposal does not comprise the concept of compounding two or more camphor substitutes into a perfume.

Typical compositions are given in the following examples merely for the purpose of illustrating my invention; the relation between parts by volume and parts by weight is the same as between cubic centimetre and gram.

EXAMPLE 1.

A plasticizing solvent was compounded from:—

5	True Neroli petal oil	35	parts by volume
	Vanillin	10	" " "
	Ethyl butyrate	30	" " "
	Ethyl pelargonate	100	" " "
	Cyclohexyl butyrate	50	" " "
	Amyl formate	20	" " "
10	Acetaldehyde	5	" " "

250 " " "

A mixture was then made with:—

	Above plasticizing solvent	10—20	parts by volume
15	Nitrocellulose $\frac{1}{2}$ sec.	10	" " weight
	Dewaxed shellac	20	" " "
	Alcohol (strength 90% by volume) q.s. for	100	" " volume
	Colouring material	q.s.	" " "

20 The mixture was stirred until a solution was obtained, with grinding if need be.

A film produced from the above composition was dry after 6 minutes

EXAMPLE 2.

25 A plasticizing solvent was compounded from:—

	Linalyl acetate	20	parts by volume
	Terpenyl acetate	10	" " "
	Geranyl acetate	10	" " "
30	Citral	10	" " "
	Eugenol	2	" " "
	Methyl cinnamate	2	" " "
	Ketone musk	3	" " "
	Alpha-ionone	3	" " "
85	Geraniol	15	" " "
	Benzylidene-acetone	5	" " "
	Citronellal	2.5	" " "
	Heliotropin	8	" " "
40	Tonkin musk tincture (3 per cent.)	9.5	" " "

100.00 " " "

A mixture was made with:—

	Above plasticizing solvent	10—20	parts by volume
45	Nitrocellulose $\frac{1}{2}$ sec.	10	" " weight
	Dewaxed shellac	20	" " "
	Alcohol (90%) q.s. for	100	" " volume
	Colouring material	q.s.	" " "

50 The mixture was stirred from time to time until dissolution took place, with grinding if need be.

A film produced from the above composition was dry after about half an hour.

EXAMPLE 3.

55 The following ingredients were compounded into a plasticizing, solvent mixture:—

	Citronellyl acetate	6	parts by volume
	Geranyl acetate	10	" " "
	Nerol	4	" " "
60	Coumarin	5	" " "
	Vetiver oil	2	" " "
	Linalyl acetate	10	" " "
	Linalyl propionate	3	" " "

	Ambrette musk	3	parts by volume
	Ketone musk	2	" " "
	Lemon oil	5	" " "
	Patchouli	1	" " "
	Heliotropine	9	" " "
	Lavender oil	6	" " "

66 " " " 70

A mixture was made from:—

	Above plasticizing solvent mixture	10—20	parts by volume
	Nitrocellulose $\frac{1}{2}$ sec.	10	" " weight
	Dewaxed shellac	20	" " "
	Alcohol (90%) q.s. for	100	" " volume
	Colouring material	q.s.	" " "

The mixture was stirred from time to time until dissolution took place with grinding if need be.

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EXAMPLE 4.

This example will illustrate a manner of compounding lower alkyl acetates.

A solvent diluent mixture was produced from:—

	Ethyl acetate	5	parts by volume
	Amyl acetate	10	" " "
	Ethyl butyrate	1	" " "
	Alcohol (95%)	54	" " "

By incorporating 20 parts by weight of dewaxed shellac, 10 parts by weight of nitrocellulose $\frac{1}{2}$ sec. and an amount of colouring material, I obtained a finger nail enamel composition having a pear smell and drying in a few minutes.

95

The "varnish" odour of acetates was no longer detectable.

With a view to plasticizing the composition, a little heliotropine might be added thereto, shifting the smell to a velvety smell of Duchess pear.

100

EXAMPLE 5.

Where ethyl acetate which has been stated to be desirable for obtaining hard films has to be employed as sole acetate, it might be compounded as follows with other solvents and a diluent:—

	Ethyl acetate	10	parts by volume
	Ethyl benzoate	10	" " "
	Ethyl cinnanthylate	2	" " "
	Alcohol (90%) saturated with benzoic acid	48	" " "

By incorporating 20 parts by weight of resins and 10 parts by weight of nitrocellulose $\frac{1}{2}$ sec. in the above mixture, I obtained a quick drying, plasticized, finger nail enamel composition having a cherry smell. The characteristic smell of ethyl acetate had disappeared completely.

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EXAMPLE 6.

	I mix together:—		
	Benzyl acetate	20	parts by volume
	Benzyl phenylacetate	2	" " "
	Cyclohexyl butyrate	5	" " "
	Amyl butyrate	10	" " "
	Ethyl acetate	13	" " "
	Vanillin	0.50	" " weight

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From 25 parts by volume of said mixture, 45 parts by volume of 95% alcohol, 10 parts by weight of nitrocellulose and 20 parts by weight of dewaxed shellac, I obtained a composition having a very pleasant smell and yielding films which dry in 8 minutes.

EXAMPLE 7.

A mixture compounded as follows:—

	Nitrocellulose $\frac{1}{2}$ sec.	10	parts by weight
10	Dewaxed shellac	10	" " "
	Ethyl orthoformate	25	" " volume
	Thyme oil	0.50	" " "
	Wild thyme oil	0.50	" " "
	Lemon oil	0.50	" " "
15	Terpineol extra	0.50	" " "
	Alcohol (95%) q.s.		
	for	100	" " "
	Colouring material	q.s.	

provided a finger nail enamel composition having a very pleasant balsamic smell.

As far as I am aware, ethyl orthoformate has not been described as yet as a diluent-solvent for nitrocellulose varnishes.

EXAMPLE 8.

25	Nitrocellulose $\frac{1}{2}$ sec.	10	parts by weight
	Dewaxed shellac	10	" " "
	Dihydrocarveyl acetate	0.80	" " volume
	Isocugenol	0.40	" " "
30	Eugenol	0.60	" " "
	Neroli	0.30	" " "
	Absolute orange blossom oil	0.20	" " "
	Coumarin	0.60	" " "
35	Bergamot	2.10	" " "
	Vanillin	0.30	" " weight
	Rhodinol	0.70	" " volume
	Isobutyl acetate	0.70	" " "
	Citronellyl formate	0.50	" " "
40	Methylnone	1.80	" " "
	Hydroxy citronellal	1.00	" " "
	Isobutyl propionate	20.00	" " "
	Alcohol (96%) q.s.		
	for	100.00	" " "
45	Colouring material	q.s.	

In the above composition, isocugenol, eugenol, coumarin, and vanillin play the part of plasticizers and have been compounded to give a pleasant smell.

A film of the above composition dried in 5 minutes.

EXAMPLE 9.

	Nitrocellulose $\frac{1}{2}$ sec.	10	parts by weight
	Dewaxed shellac	10	" " "
55	Amyl formate	0.50	" " volume
	Amyl butyrate	0.50	" " "
	Ethyl butyrate	0.50	" " "
	Alpha-amyl dihydrocinnamyl alcohol	1.50	" " "
60	Phenyl butyl acetate	1.00	" " "
	Bourbon Ylang-Ylang	2.20	" " "
	Dimethyloctyl acetate	1.80	" " "

	Alpha-ionone	2.00	parts by volume
	Isobutyl-propionate	20.00	" " "
	Alcohol (96%) q.s.		
	for	100.00	" " "
	Colouring material	q.s.	

Ylang-Ylang and ionone in addition to providing valuable perfume components, play the part of plasticizers.

EXAMPLE 10.

The plasticizer-solvent mixture was compounded as follows:—

	Amyl acetate	5	parts by volume
	Ethyl acetate	45	" " "
	Amyl valerianate	100	" " "
	Acetaldehyde (50%)	20	" " "
	Ethyl nitrate	10	" " "
	Chloroform	10	" " "

By incorporating 20 to 30 parts by weight of a film-forming base (nitrocellulose $\frac{1}{2}$ sec. resin) in 20 to 30 parts by volume of the above mixture and the complement of ethyl alcohol (90—96%) to 100 parts by volume, I obtained a composition which had a fresh, pungent scent of apple.

A film dried in 3 to 5 minutes.

It should be understood that the foregoing examples are simply given as typical for illustrating my invention, and a wide number of other formulas can be adopted.

It is believed that with this invention, many advantages are secured and the following objects *inter alia* are attained:—

1. The component and proportions thereof enable of providing a homogeneous mixture as is required for a proper strength of finger nail enamel films.

2. Nitrocellulose and resins are wholly dissolved and plasticized.

3. It is possible to provide a wide range of colours and pleasant scents which can thus be selected according to fashion.

4. The components are compatible together and are not altered as they age.

5. The components are compatible with pigments and colouring materials as usually employed.

6. The films obtained are flexible, strong and adhesive.

7. The rate of evaporation can be controlled to be quick, average or slow.

What I claim is:—

1. A finger nail enamel composition obtained by mixing together components comprising 10—30 parts by weight of a film forming base which is a cellulose derivative or a mixture of a cellulose derivative and a resin, about 10—30 parts by volume of a mixture of at least two odoriferous substances compounded into a perfume providing a solvent for the film-forming base, the major portion of said mixture consisting of substances which have not less than 7 carbon atoms and contain at least one methyl group and are selected from the class of esters, aldehydes, ketones, alcohols and essential oils,

- and about 40—80 parts by volume of a diluent which is an aliphatic alcohol having from 2 to 4 carbon atoms, or a propionic acid ester, parts by weight and parts by volume being expressed in the manner hereinbefore defined.
- 5 2. A finger nail enamel composition as claimed in claim 1, wherein the diluent is ethyl alcohol, preferably in the form of commercial alcohol.
- 10 3. A finger nail enamel composition as claimed in claim 1 or claim 2, wherein the film forming base comprises nitrocellulose and at least one resin of the class of fingernail enamel natural and artificial resins.
- 15 4. A finger nail enamel composition as claimed in any one of the foregoing claims which contains ethyl orthoformate as a component.
- 20 5. A finger nail enamel composition as claimed in any one of the foregoing claims, which contains isobutyl propionate as a component.
6. A finger nail enamel composition as claimed in any one of the foregoing claims, wherein the odoriferous substances contain a 25 nitro tertiary-butyl xylene.
7. A finger nail enamel composition as claimed in any one of the foregoing claims, wherein the odoriferous substances comprise in major proportion substances from the class 30 of acyclic terpenic alcohols, lower aliphatic acid-esters thereof and corresponding aldehydes.
8. A finger nail enamel composition, substantially as described in the examples. 35

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